Interaction Energy of Nitrogen Molecules

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The interaction energy between two nitrogen molecules is an important basic property needed to determine certain input data required for a real-gas analysis of aerodynamic flows. An accurate representation of the rigid-rotor interaction potential has been constructed by combining the ab initio data and the experimental second virial data to determine the interaction energy in the van der Waals region in a manner consistent with the physics of the interaction. The construction of the potential energy surface is based on the potential function developed by Tang and Toennies for the atom-atom van der Waals interaction.

Extensive electronic structure calculations have been performed to determine the interaction energy of two rigid nitrogen (N_2) molecules, using the coupled-cluster singles and doubles approach, including a perturbational estimate of the triple excitations (denoted CCSD(T)). Full configuration-interaction benchmark studies have shown that the CCSD(T) method accurately determines the electron correlation for systems that are reasonably well described by a single reference. The principal limitation in determining the interaction energy will be basis set incompleteness. The ab initio results define the potential energy surface at small intermolecular separation, as well as the anisotropic behavior of the interaction energy for large intermolecular separations.

Adapting previous work, the strength and slope of the repulsive potential are adjusted in order to increase the well depth to reproduce the measured values of the second virial coefficient B(T). Since the contribution to B(T) from repulsive orientations is small, the virial coefficient is relatively insensitive to errors in the potential energy of these orientations. Hence, the physics of the interaction must be taken into account to obtain a realistic potential energy surface from a fit to measured data for the virial coefficient. The present interaction potential is more anisotropic than the potential of Van der Avoird, Wormer, and Jansen. For example, the angular contribution from the first-order quantum-mechanical correction to B(T) is larger using the present potential, with the difference rising to about 30% at the lowest temperature (75 kelvin) of the virial measurements.

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